1999

Annual *Data Quality* Report

for the

Monitoring and Laboratory Division's
and
Local Districts' Air Monitoring Networks

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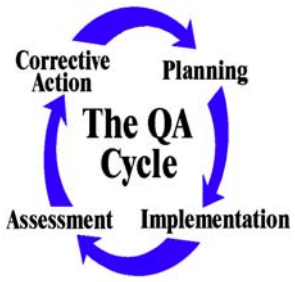
I. INTRODUCTION

The purpose of this report is to provide users of ambient air quality data with a summary of the quality of the 1999 data in quantifiable terms. This is the second edition of this document. It presents an overview of various quality assurance and quality control activities found in the previous report with several new additions. The tables used to depict the data provide a summary of the network of air monitoring sites in California. New topics for this volume include: reports of precision data, information about quality control reports, production figures from the Standards Certification Laboratory, and the status of standard operating procedures. Future documents will include reports on additional quality assessment and quality control parameters.

The ARB's mission is to promote and protect public health, welfare, and ecological resources through effective and efficient reduction of air pollutants while recognizing and considering the effects on the economy of the State. The Monitoring and Laboratory Division (MLD) provides a key element of that mission through collecting and reporting on quality information on a large number of pollutants and for a vast air monitoring network. The MLD, directed by State law, conducts ambient air monitoring in support of ARB divisions, local air pollution control and air quality management districts, and the United States Environmental Protection Agency (U.S. EPA). Monitoring programs include gaseous pollutants, particulate matter, toxic air contaminants, non-methane hydrocarbons, pesticides, consumer products, meteorological parameters, and visibility. Data from these monitoring sources provide the means to determine the nature of the pollution problem and assess how well control programs are working. The Division mission includes supporting the regulatory and assessment programs of the Board.

It is the goal of MLD to provide accurate, relevant, and timely measurements of air pollutants and their precursors to support California's Air Quality Management Program for the protection of public health. The Quality Assurance Section (QAS) conducts various quality assurance activities to ensure that data collected comply with procedures and regulations set forth by the U.S. EPA and can be considered good quality data and data-for-record.



What is quality assurance? Quality assurance is an integrated system of management activities that involves planning, implementing, assessing, and assuring data quality through a process, item, or service that meets users needs for quality, completeness, representativeness and usefulness. Known data quality enables users to make judgements about compliance with air quality standards, air quality trends and health effects based on sound data with a known level of confidence. The objective of quality assurance is to provide accurate and precise data, minimize data loss due to malfunctions, and to assess the validity of the air monitoring data to provide representative and comparable data of known precision and accuracy.

Quality assurance is composed of two activities: quality control and quality assessment. *Quality control* is composed of a set of internal tasks performed routinely at the

instrument level that ensures accurate and precise measured ambient air quality data. Q*uality control* tasks address sample collection, handling, analysis, and reporting. Examples include calibrations, routine service checks, chain-of-custody documentation, duplicate analyses, development and maintenance of standard operating procedures, and routine preparation of quality control reports.

Quality assessment is a set of external, quantitative tasks that provide certainty that the quality control system is satisfactory and that the stated quantitative programatic objectives for air quality data are indeed met. These external tasks are performed by staff independent of data generators. Tasks include conducting regular performance audits, on-site system audits, interlaboratory comparisons, and periodic evaluations of internal quality control data. Table 1 illustrates the types of performance audits currently performed by the ARB for each air monitoring program. Field and laboratory performance audits are the most common. System audits are performed on an as-need basis or by request. Whole air sample comparisons are conducted for the non-methane hydrocarbon program, with plans to extend it to the toxic air contaminants program in 2000.

***Table 1*. Audits Performed for Each Air Monitoring Program in 1999**

Air Monitoring Program	Field Performance Audit	Laboratory Performance Audit	System Audit	Whole Air Audit
Gaseous Pollutants	X	X	FUTURE	
Particulate Matter	X	X	X	
Toxic Air Contaminants	X	X		FUTURE
Non-Methane Hydrocarbons	X	X	FUTURE	X
Pesticides	X			
Consumer Products		X		
Meteorology	X			

II. QUALITY CONTROL AND QUALITY ASSESSMENT

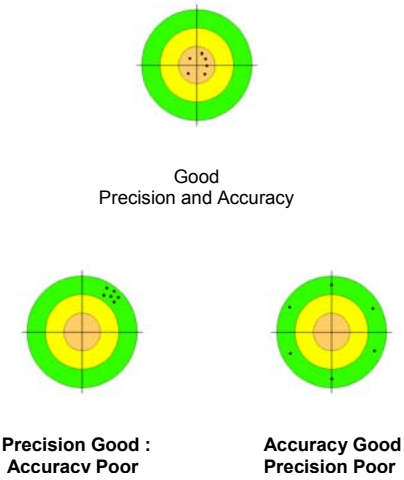
The Quality Assurance Section (QAS) supports all ambient monitoring programs undertaken by the Division, including gaseous criteria pollutants, particulate pollutants, toxic air contaminants, non-methane hydrocarbons, pesticides, consumer products, and meteorology, which are run by the ARB and local and private air monitoring agencies. There are approximately 230 air monitoring sites in 14 separate air basins operating in California.

Appendix A provides information about the air monitoring network (i.e., sampling schedules, number of instruments, collection/analysis method, etc.). The information in Appendix A is also available at the following Internet site under Air Monitoring Activities at http://www.arb.ca.gov/aaqm/qmosqual/qmosqual.htm.

Information about each air monitoring station audited by the ARB is available at http://www.arb.ca.gov/aqdas/siteinfo.htm. This web site is new and includes maps of each site, latitude and longitude coordinates as determined by GPS, site photos, precision and accuracy data, and a detailed survey of the physical parameters and

conditions at each site. The site surveys list in-depth monitoring information such as traffic descriptions, calibration dates, distances to trees and obstacles, and residence times. This site also includes an area for district precision and accuracy reports. These reports are available on a limited basis to district staff.

The air quality monitors collect data in both real-time and on a time integrated basis. The data are used to define the nature, extent, and trends of air quality in the State; to support programs required by State and federal laws; and to track progress in attaining air quality standards. The precision and accuracy necessary depends on how the data will be used. The illustration to the right shows the relationship between precision and accuracy. Data that must meet specific requirements (i.e., criteria pollutants) are referred to as controlled data sets. Criteria for the accuracy, precision, completeness, and sensitivity of the measurement in controlled data sets must be met and documented.



Air Quality Data Actions (AQDAs) are a key tool used by the QAS to confirm the data set meets the established limits. They are initiated upon a failed audit and resolved after a review of calibrations, precision checks, and audit results. The AQDA must confirm that an analyzer/sampler has operated within ARB's control limits of +/-15 percent (+/-10 percent for PM10 and +/-5% for PM2.5), or for siting or temperature conditions otherwise, further action is taken.

Data without formal data quality objectives (i.e., toxics) are called *descriptive data sets*. The data quality measurements are made as accurately as possible in consideration of how the data are being used. Quantified quality assessment results describe the measurement variability in standard terminology, but no effort is made to confine the data set to values within a predetermined quality limit.

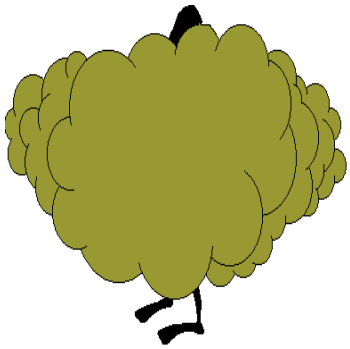
The ARB's Quality Assurance Program is outlined in a six-volume *Quality Assurance Manual*. The volumes, listed below, guide the operation of the quality assurance programs used by the ARB, local districts, and private industry in California.

Volume I	Quality Assurance Plan
Volume II	Standard Operating Procedures for Air Quality Monitoring
Volume III	Laboratory Methods and Operations
Volume IV	Air Quality Data Processing (Not Available)
Volume V	Audit Procedures Manual
Volume VI	Standard Operating Procedures for Stationary Source Emission Monitoring and Testing

Volumes I, II, III, and V, and parts of VI are available on the Internet at http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm. Volume I lists the

data quality objectives and describes quality control and quality assessment activities used to ensure that the data quality objectives are met.

A. Gaseous Pollutants



Ambient concentrations of carbon monoxide (CO), nitrogen dioxide (NO2), ozone (O3), sulfur dioxide (SO2), and hydrogen sulfide (H2S) are continuously monitored by an automated network of stations run by MLD and the districts. Exposure to these pollutants cause adverse health effects which include respiratory impairment, fatigue, permanent lung damage, and increased susceptibility to infection in the general population. Non-criteria pollutants such as methane (CH4) and total hydrocarbons (THC) are also monitored continuously as precursors for criteria pollutants to help ensure the ambient air quality standards are met. Gaseous criteria pollutant data, including non-criteria pollutants CH4 and THC, are a controlled data set and are subject to meeting mandatory regulations.

Accuracy (field): Annually, the QAS conducts field through-the-probe (TTP) performance audits for gaseous pollutants to verify the system accuracy of the automated methods and to ensure the integrity of the sampling system.

Accuracy is represented as an average percent difference. The average percent difference is the combined differences from the certified value of all the individual audit points. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in statistical analysis if the audit was deleted due to an AQDA that resulted in data deletion.

Overall, the responses of the individual analyzers indicate that as a whole, the network is providing accurate data. Ninety-six percent of the instruments in 1999 were found to be operating within the ARB's control limits. The most common causes for audit failure are malfunctions within the instrument and leaks in the sampling system. The instruments operating outside of the control limits resulted in 1,038 days of deleted data. Tables A1 and A2 summarize the 1999 performance audit results for the criteria and non-criteria pollutants.

Further information about the air monitoring systems and the audit procedures are available at http://www.arb.ca.gov/aaqm/qmosqual/sysaudit/criteria/qa_gas.html.

Table A1. **1999 Results for Criteria Pollutants Performance Audits Conducted by ARB**

Pollutant	Number of Analyzers Audited	Average % Difference	Probability Limits 95%UL	95%LL
CO	63	0.6	8.0	-6.8
NO2	85	-3.3	5.2	-11.8
O3	147	-2.5	4.8	-9.8
SO2	27	-1.2	8.1	-10.5
H2S	8	2.4	12.9	-8.1

Source: Quality Assurance Section, Accuracy Estimates

Table A2. **1999 Results for Non-Criteria Pollutants Performance Audits Conducted by ARB**

Pollutant	Number of Analyzers Audited	Average % Difference	Probability Limits 95%UL	95%LL
CH4	22	-1.1	9.0	-11.2
THC	15	1.3	17.7	-15.1

Source: Quality Assurance Section, Accuracy Estimates

MLD also participates in the U.S. EPA's National Performance Audit Program (NPAP). The results of the NPAP audits, available upon request, are calculated and compiled by the U.S. EPA. The audits differ from our TTP audits in that the gas is introduced at the back of the instrument instead of the probe.

Precision (field): Precision checks are performed by site operators on a nightly basis to confirm the linear response of the instrument. The zero precision check confirms the instrument's ability to maintain a stable reading. The span precision check confirms the instrument's ability to respond to a known concentration of gas.

Annually, the QAS conducts a precision data analysis as an overall indicator of data quality. The analysis addresses three parameters: precision data submission, precision data validity, and a combination of the two referred to as data usability rates. The precision performance goal for all three parameters is 85%. The submission rate is the number of precision points submitted for a pollutant divided by the expected number of bi-weekly submissions. Data validity is the percent difference of the actual and indicated values of each precision check. These differences should not exceed $\pm$15% for gaseous analyzers. Usable data rates are determined by multiplying the data submission and data validity rates; and indicate the completeness of verifiable air quality data on the official database. Overall, the precision data submitted met the design criteria; however, because of low submission rates, the 85% performance goal for usable data rates were not met. Table A3 shows the Statewide submission, validity, and usable data rates for each pollutant. For a more detailed description of the usability data rates for each District, please refer to Appendix B.

Table A3. **1999 Criteria Pollutants Precision Analysis Results for California**

Pollutant	Submission Rate	Validity Rate	Usable Rate
CO	79%	99%	79%
NO2	72%	98%	71%
O3	79%	96%	75%
SO2	74%	92%	68%
H2S	16%	100%	16%

Source: Quality Assurance Section, Precision Data Analysis

B. Particulate Matter

Particulate Sampler

Particulate matter monitoring is conducted using both manual and continuous type samplers. Manual samplers are operated on a six-day sampling schedule for PM10, and a similar, or more frequent schedule, for PM2.5. ARB's particulate program also includes total suspended particulates (TSP) sulfate and lead (Pb). Respirable particulate matter (PM10) and fine particulate matter (PM2.5) increase the chance of respiratory disease, lung damage, cancer, and premature death. Particulate matter is a controlled data set and as such is subject to formal data quality objectives and federal and State regulations. Visit the Particulate Matter Monitoring home page for more information at: http://www.arb.ca.gov/aaqm/partic.htm.

Accuracy (field): The accuracy of particulate samplers is determined using a certified variable orifice (PM10 and TSP), or a calibrated mass flow meter (dichotomous, TEOM, BAM, and PM2.5 samplers) that is certified against a NIST-traceable flow device or calibrator. Since accurate measurement of particulate matter is dependent upon flow rate, the ARB conducts annual flow audits at each site. The average percent difference between the sampler flow rates and the audit flow rates represents the combined differences from the certified value of all the individual audit points for each sampler. The upper and lower probability limits represent the expected flow rate accuracy for 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in the statistical analysis shown here if the audit was deleted due to an AQDA that resulted in data deletion.

Overall, the flow audit results indicate that the network is providing accurate flow rate data. Ninety-three percent of the instruments audited operated within the ARB's control limits. Instruments operating outside the control limits typically had an improper set-point of the mass flow controller or drift that was not discovered. Under normal operation, the set-point of the mass flow controller should compensate for a change in temperature and pressure. A total of 2,439 days of data were deleted in 1999 due to instruments operating outside of ARB's control limits. The 1999 performance audit results are listed below in Table B1.

***Table B1*. 1999 Results for Particulate Sampler Performance Audits Conducted by ARB**

Pollutant	Number of Samplers Audited	Average % Difference	Probability Limits 95%UL	95%LL
PM2.5	94	-1.1	2.6	-4.8
PM10	143	-0.3	5.9	-6.5
PM10 Partisol	4	-3.1	2.5	-8.7
Dichotomous	18	0.1	8.4	-8.2
TEOM	33	-1.4	4.4	-7.2
BAM	3	-5.2	5.2	-15.6
TSP	15	-1.5	7.9	-10.9
Pb	17	0.0	8.4	-8.4

Source: Quality Assurance Section, Accuracy Estimates

Precision (field): Precision data for non-continuous particulate samplers is obtained by collocated sampling, the simultaneous operation of two identical samplers placed side-by-side whose filters are analyzed by the same laboratory. In 1999, collocated high-volume SSI samplers were operated at Bakersfield and Visalia and collocated dichotomous samplers at Bakersfield and Fresno. Collocated samplers are located at selected sites and are intended to represent the network precision on the whole. Data validity is based on the percent difference of the mass concentrations of the two samplers.

Particulate samplers, collocated PM10, dichotomous, and TSP samplers must have mass concentrations greater than or equal to 20μg/m^3 to be used in data validity calculations. The difference between the mass concentrations must be no greater than 5μg/m^3. If the mass concentrations are greater than 80μg/m^3, the difference must be within $\pm$7% of each other. For Pb samplers, both mass concentrations must be greater than or equal to 0.15μg/m^3 to be used in data validity calculations. For collocated PM2.5 samplers, data validity is based upon the sample's coefficient of variation, which cannot exceed 10%. Both sample masses must also be greater than or equal to 6μg/m^3 to be considered a valid sample in data validity rate calculations.

Continuous TEOM and BAM precision is based on the comparison of the sampler's/analyzer's indicated and actual flow rates. The differences between the flow rates must be within +/-15% of each other. Overall, the precision data that were submitted met the data validity rate performance goal of 85%. However, none of the pollutants met the submission and usable data rate performance goals. This is the first year that the submission rate performance goal was not met for any particulate pollutant. The particulate sampler precision analysis results for 1999 are available in Table B2. For a more detailed description of the usability data rates for each District, please refer to Appendix B.

Table B2. **1999 Particulate Sampler Precision Analysis Results for California**

Pollutant	Submission Rate	Validity Rate	Usable Rate
PM2.5	42%	98%	42%
PM10	54%	85%	46%
PM10 Partisol	13%	85%	11%
Dichotomous	0%	NA	NA
TEOM	29%	89%	26%
BAM	0%	NA	NA
TSP	84%	69%	58%
Pb	33%	100%	33%

Source: Quality Assurance Section, Precision Data Analysis

Accuracy (lab): Performance audits for PM10 mass analysis programs include an on-site check and assessment of the PM10 filter weighing balance, relative humidity and temperature sensors, and their documentation. The performance audits conducted in 1999 found that of the 12 District programs audited, three failures were identified. However, due to good laboratory QC practices (duplicate weighings, balance calibrations), no data were affected. Table B3 summarizes the performance audit findings.

Table B3. **1999 PM10 Particulate Matter Mass Analysis Performance Audits**

District	Conducted	Pass/Fail
Great Basin Unified APCD	October	Passed
Mojave Desert AQMD	February	Passed
Monterey Bay Unified APCD	March	Passed
North Coast Unified AQMD	April	Passed
No. Sierra AQMD	September	Failed; Relative Humidity Check
No. Sonoma Co. APCD	June	Passed
Placer Co. APCD	February	Passed
Sacramento Metropolitan AQMD	October	Failed; Balance Check
San Luis Obispo APCD	March	Failed; Temperature Check
Santa Barbara Co. APCD	August	Passed
Siskiyou Co. APCD	April	Passed
Ventura Co. APCD	May	Passed

Laboratory audits for PM2.5 mass analysis programs include an annual on-site check and review of a monitoring organization's entire program. The total measurement system is reviewed annually (sample collection, sample analysis, data processing, etc.). The audits include a review of staff qualifications, procedures, facilities, and documentation to assure compliance with federal air quality monitoring, quality assurance, and data reporting regulations. Laboratories supporting the PM2.5 mass analysis program must first complete a pre-certification process that includes a questionnaire, an on-site visit, and a performance audit of the laboratory's microbalance and relative humidity (RH) and temperature sensors. Pre-certification standards must

be met before the laboratory is able to submit PM2.5 data to the U.S. EPA's Aerometric Information Retrieval System (AIRS)-Air Quality Subsystem (AQS). All laboratories met the pre-certification conditions. Full system audits were initiated thereafter. Three PM2.5 system audits were conducted in 1999. The system audit findings concluded that the South Coast Air Pollution Control District, the Bay Area Air Quality Management District, and the ARB's PM2.5 mass analysis program satisfied the U.S. EPA regulations, and that the data were of good quality and should be considered data-for-record.

Laboratory audits are also conducted using NIST-traceable filter standards for nitrate (NO3-), sulfate ($SO4^{-2}$), chloride (Cl-), ammonium (NH4+), and potassium (K+). The ARB's Northern Laboratory Branch participated in the PM10 ions laboratory performance audit conducted in June 1999. The results for all compounds were within the targeted +/-20% limits established for the audit.

MLD also participates in the field and laboratory NPAP programs for PM10 and dichotomous. The U.S. EPA compiles the NPAP audit results. The results are available upon request from the U.S. EPA. The federal audit program covers only a portion of the PM10 network sites in California. The ARB audit results; however, are compared to the NPAP results to understand and improve the audit program.

Precision (lab): Laboratories perform various quality control tasks to ensure that quality data are produced. Tasks include duplicate weighings on exposed and unexposed filters, replicate analysis on every 10^{th} filter, and a calibration of the balance before each weighing session. Filters are also visually inspected for pinholes, loose material, poor workmanship, discoloration, non-uniformity, and irregularities, and are equilibrated in a controlled environment for a minimum of 24 hours prior to pre- and post-sample weighing. Weighings must also be conducted in a controlled environment. If room conditions are not within the established U.S. EPA control limits, no weighings are done until 24 hours after the proper environment is re-established.

In 1999, there were no occurrences in which ARB's laboratory's balance room was outside of control limits. However, one TSP replicate weighing was found to be outside of ARB's established control limits. The filter was reweighed and determined invalid due to loss of particulate matter between weighings. The analytical precision results indicate that ARB is providing precise particulate matter data. Tables B4 and B5 show the unexposed and exposed filter replicate results for ARB's laboratory in 1999.

***Table B4*. 1999 Summary of ARB's Unexposed Filter Mass Replicates**

QC Check	PM2.5	PM10	Dichotomous	TSP
# of pre-weighed filters	3345	4813	1800	1023
# of replicates analyses	388	604	237	125
% replicates weighing conducted	11.6	12.5	13.2	12.2
# of replicates out of range	0	0	0	0

Source: Inorganics Laboratory Section, Quality Control Report

Table B5. **1999 Summary of ARB's Exposed Filter Mass Replicates**

QC Check	PM2.5	PM10	Dichotomous	TSP
# of pre-weighed filters	2772	4232	2370	646
# of replicates analyses	311	499	257	74
% replicates weighing conducted	11.2	11.8	10.8	11.5
# of replicates out of range	0	0	0	1

Source: Inorganics Laboratory Section, Quality Control Report

C. Toxic Air Contaminants

Stainless Steel Toxics Canister

The ARB established an ambient volatile organic compound (VOC) toxic monitoring network in major urban areas of the state in 1985 to determine the average annual concentrations of toxic air contaminants. The recently enacted State law required that the ARB confirm the presence of compounds in the ambient air that were candidates as Toxic Air Contaminants. Under the current sampling schedule, ambient air is collected at each of the 17 sampling stations in a stainless steel canister every 12 days for a 24-hour period. The samples are analyzed by the Northern Laboratory Branch. Toxic air contaminants include aromatic, halocarbon semi volatiles, and oxygenated compounds.

Toxic particulate samples are also collected and analyzed for toxic air contaminants to support the California Toxic Air Contaminant Identification and Control program. By using a low-flow, multi-channel sampler, capable of sampling onto filters or cartridges, ambient air is collected and analyzed for carbonyl and polycyclic aromatic hydrocarbons (PAH) compounds and toxic metals. The quality of the air toxic data set is governed by a series of quality assurance activities, including audits. However, because this is a descriptive data set, no mandatory corrections are made to the data based on audit results. The laboratory and monitoring staff are made aware of any exceedance found during and audit, and every effort is made to ensure that the data collected is as accurate as possible.

The audit programs contained two elements in 1999: the TTP audits and laboratory audits. The audit results are available on the Internet at the following address: http://www.arb.ca.gov/aaqm/toxics.htm, including several papers that discuss these elements of the QA program in detail.

Accuracy (field): Annual TTP performance audits were conducted for volatile organic compounds at each air toxic site to assess the accuracy of the total measurement system. System errors can include contamination during transport, artifacts created by the sample pump or the probe, and laboratory bias. The 1999 audit results indicated exceedances of the audit criteria (+/-20%) for several compounds. The results for 1999 are shown in Table C1. The values represent the average percent difference for each

compound from all audits conducted at ARB sites. The TTP Toxics audit program was suspended for calendar year 2000 due to resource constraints, but will resume in 2001.

A whole air sampler performance check will be added in 2000 to compare the analytical methods used by all the laboratories that measure ambient concentrations of toxic compounds. A specially designed sampler will draw ambient air for 24 hours, filling up to 10 canisters at a time, to an approximate pressure of 14 pounds per square inch gauge (psig) each. This replicates a normal sample duration and pressure. A canister will be sent to each participating laboratory for analysis. The laboratories will follow their standard operating procedures in assaying the contents and report their results to the QAS, who in turn, will compare the results to the other participating laboratories. This will be the first time the check will be performed for toxic air contaminants.

***Table C1*. 1999 Toxic Air Contaminants TTP Audit Results for California's Toxic's Network**

	TTP	
Compound	Avg % Diff	Std Dev
Benzene	4.6	14.4
1,3-Butadiene	-33.1	8.1
Carbon Tetrachloride	-6.3	13.3
Chloroform	-17.9	12.9
ortho-Dichlorobenzene	-20.5	21.7
Ethylbenzene	-24.0	20.3
Methyl Chloroform	-16.7	30.3
Methylene Chloride	11.1	9.8
Perchloroethylene	-27.6	24.7
Styrene	-0.6	25.0
Toluene	-4.2	15.4
Trichloroethylene	-3.3	7.2
m/p-Xylene	-27.3	23.2
o-Xylene	-13.2	25.8

Flow audits of the toxic metal and carbonyl sampler (shown right) are conducted annually at each site to ensure the accuracy of measuring toxic metals and carbonyl compounds. Flow rates are a determining factor in calculating concentration and are included as part of the quality assurance program.

Toxic metals and carbonyl sampler

Overall, the 1999 results indicate that the samplers maintained stable flows. Ninety-seven percent of the instruments audited operated within the ARB's control limits of +/-15% from true. Although a descriptive data set, AQDAs are issued based on the operating parameters of the sampler. Corrections are made to the data if an audit is found to be outside ARB's control limits. One AQDA was issued for the pollutant Cr6+, which resulted in 117 days of data to be deleted.

Table C2 shows the differences from the certified value of the individual audit points for each pollutant. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in the statistical analysis shown here if the audit was deleted due to an AQDA.

Table C2. **1999 Results for Toxic Air Sampler Performance Audits Conducted by ARB**

Pollutant	Number of Samplers Audited	Average % Difference	Probability Limits 95%UL	95%LL
Cr6+	13	2.2	6.5	-2.1
Total Metals	12	1.4	7.0	-4.2
Aldehydes	13	-1.8	5.3	-8.9

Source: Quality Assurance Section, *Accuracy Estimates*

Accuracy (lab): Laboratory performance audits were conducted semi-annually to determine the accuracy of a laboratory's ability to measure ambient VOC concentrations. The laboratory performance audit results for 1999 continued to show a significantly low response for methyl chloroform. ARB's laboratory was asked to investigate the potential cause of the low response and found that the primary gas chromatograph system was malfunctioning. The system has since been refurbished. The 1999 audit results are shown in Table C3. The percent difference presented in the table represents the difference between the laboratory's observed level from the NIST certified value.

The toxic metals laboratory performance audit results, shown on Table C4, indicate that the laboratory is accurately identifying these compounds. The upper and lower probability limits show the expected accuracy for 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site.

***Table C3*. ARB's 1999 Toxic Air Contaminants Laboratory Performance Audit Results**

Compound	Laboratory	
	% Diff	Std Dev
Benzene	-8.2	NA
1,3-Butadiene	-3.1	NA
Carbon Tetrachloride	-5.6	NA
Chloroform	-26.3	NA
ortho-Dichlorobenzene	9.1	NA
Ethylbenzene	-18.4	NA
Methyl Chloroform	50.0	NA
Methylene Chloride	-11.2	NA
Perchloroethylene	18.2	NA
Toluene	13.8	NA
Trichloroethylene	-10.2	NA
m/p-Xylene	-8.0	NA
o-Xylene	0.0	NA

NA= Standard deviation not calculated; 1 audit conducted

***Table C4*. ARB's 1999 Toxic Metals Laboratory Performance Audit Results**

Pollutant	Number of Audits	Average % Difference	Probability Limits	
			95%UL	95%LL
Arsenic	4	0.6	12.9	-11.7
Cadmium	4	-3.6	11.2	-18.4
Lead	4	7.2	27.2	-12.8

Precision (lab): A variety of tasks are performed to ensure the precision of toxic air contaminants data. To assess the analytical precision for method MLD057-butadiene and benzene, system blanks and duplicate analyses are performed. System blanks consisting of nitrogen compressed gas serve as an instrument check before sample analysis. For 1999, all blank samples performed were below the butadiene and benzene detection limits. Duplicate analyses were performed on 10% of the samples analyzed by method MLD057. The maximum allowable percent difference for the duplicates is 15%. Duplicate data not meeting the criterion are deleted from the database. All samples analyzed on the same day in which duplicate analyses exceed the criteria limit are also deleted from the database. Affected samples are re-analyzed. In 1999, the calculated percent differences of all duplicate samples whose concentrations were greater than five times the published LODs, were below the maximum allowable value of 15%.

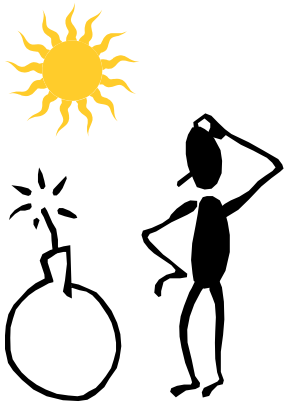
System blanks and duplicate analyses are also performed for method MLD050-MTBE to ensure analytical precision. In 1999, all system blanks were below the Methyl Tertiary-Butyl Ether (MTBE) detection limit of 0.3 ppb. Duplicate analyses were performed on 10% of the samples analyzed by method MLD050. The maximum allowable percent difference for the duplicates is 15%. Duplicate data not meeting the criterion are

deleted from the database. All samples analyzed on the same day in which duplicate analyses exceed the criteria limit are also deleted from the database. Affected samples are re-analyzed. All duplicate data for 1999 were below the maximum allowable value of 15%.

Stainless steel canisters used to collect ambient air samples are also checked for contamination. One canister per batch of eight was assayed to ensure values were below the limit of detection. Canisters are analyzed for aromatic and halogenated hydrocarbons. In 1999, a total of 178 canisters were analyzed for contamination. Of those, 7 failed the cleanliness check. All canisters represented in the batch of a failed check were re-cleaned and were below the cleanliness criteria. Overall, the network is providing precise toxic air contaminants data. Due to the amount of precision data available, only a portion of the precision data are presented.

D. Non-Methane Hydrocarbons

Photochemical Assessment Monitoring Stations



In 1989, ARB began a routine seasonal sampling program to gather information about non-methane hydrocarbon (NMHC) species such as ethane and propane, in high ozone areas. Federal regulations require states to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan monitoring networks in areas designated as serious or higher for ozone. Monitoring is to continue until the ozone standard is reached. PAMS sites collect data on ozone, oxides of nitrogen, real-time total NMHC, speciated hydrocarbons, carbonyls, and various ground level and aloft meteorological parameters. This is a descriptive data set. There are currently no mandatory data quality objectives or regulations for the data; however, much effort is expended to ensure that accurate data are collected and the analyzers are operating within ARB's audit standards of +/-20%. The errors in this data set are simply described here and on the ARB's Internet sites.

Accuracy (field): Performance audits have been incorporated into the PAMS program. Three types of hydrocarbon performance audits are conducted (laboratory, TTP sampler, and TTP continuous analyzer) that support the canister-type collection system and the real-time analyzers. A cross-check is also run by the QA staff that allows all laboratories to compare their results from a *whole air sample* representing an identical parcel of air. The whole air sample element of the QA program was added after the 1997 South Coast Ozone Study and uses a system developed by QA staff. Staff presented a paper on the program at the 2000 International Symposium on the Measurement of Toxic and Related Air Pollutants. A copy of the paper as well as other information about the PAMS QA program is available on the Internet at the following address: http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/qa_nmhc.html.

Laboratory performance audits are conducted annually to assess the laboratorys' ability to measure ambient levels of hydrocarbons. *TTP Sampler* performance audits are conducted annually at each monitoring site to assess the integrity of the sampling, analysis, and transport system. The average percent difference represents the

combined differences from the certified value for all the sites and laboratories audited. Based on the results, the PAMS network is performing well. Individual laboratory audit results were also provided to them. The continued variability in the responses for ethane is caused by one laboratory. Also, several laboratorys' reported higher values than the certified value for 3-methylhexane. The laboratories exceeding the U.S. EPA's ±20% control limits were asked to investigate the deviation. As would be expected, the TTP Sampler audits have greater bias than the laboratory audits. The 1999 *Laboratory* and *TTP Sampler* audit results are shown in Table D1.

Table D1. **1999 TTP Sampler and Laboratory NMHC Audit Results for California's PAMS Network**

	TTP			Laboratory	
Compound	Avg % Diff	Std Dev	Compound	Avg %Diff	Std Dev
Ethane	27.8	50.9	Ethane	-5.5	19.8
Ethene	6.5	7.9	Propane	-1.4	3.1
Propane	15.5	38.6	Propene	-1.4	3.5
Propene	14.5	9.3	Isobutane	-1.6	5.3
Butane	2.5	23.0	Butane	0.1	5.9
Butene	-4.4	9.5	Isobutylene	-7.9	9.2
2-Methylbutane	5.9	5.6	Isopentane	3.3	2.5
Pentane	5.5	11.7	Pentane	3.8	3.5
2,3-Dimethylbutane	3.4	6.2	1-Pentene	0.3	2.0
2-Methylpentane	9.1	8.6	Hexane	0.4	5.9
Hexane	3.5	5.4	Benzene	-0.2	5.7
Methylcyclopentane	7.6	5.4	Octane	1.6	4.9
Benzene	1.9	5.6	Toluene	-3.3	7.0
3-Methylhexane	27.0	14.9	o-Xylene	-3.5	6.9
2,2,4-Trimethylpentane	7.8	8.0	Decane	-2.8	4.1
Methylcyclohexane	10.6	6.8			
Toluene	0.6	9.0			
Octane	5.9	6.4			
Ethylbenzene	-1.9	6.1			
p-Xylene	-3.6	7.0			
o-Xylene	-0.6	10.8			
1,2,4-Trimethylbenzene	-1.2	20.8			
Decane	4.0	13.4			

The *Whole Air Sampler* performance checks complement the TTP and laboratory audits and involve all the laboratories that measure ambient concentrations of hydrocarbons. A specially designed sampler draws ambient air for 3 hours, filling up to 10 canisters at a time, to an approximate pressure of 14 pounds per square inch gauge (psig) each. This replicates a normal sample duration and pressure. A canister is sent to each participating laboratory for speciated NMHC analysis. The laboratories follow their standard operating procedures in assaying the contents and report their results to the QAS. As can be seen below in Figure D1, the laboratory responses compared well for most compounds. If a laboratory's response for a compound was significantly different from the other laboratories, the laboratory was asked to investigate the cause. The results for ethane, which were of concern in the TTP audits, were relatively good with very little variation in the whole air sample. The QAS plans to track this anomaly to determine the difference between the two audits. The whole air comparison check results are available to view on the Internet at the following address: http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/whole/wholetable.htm.

Figure D1. **1999 Whole Air Comparison Check (Continued on next page)**

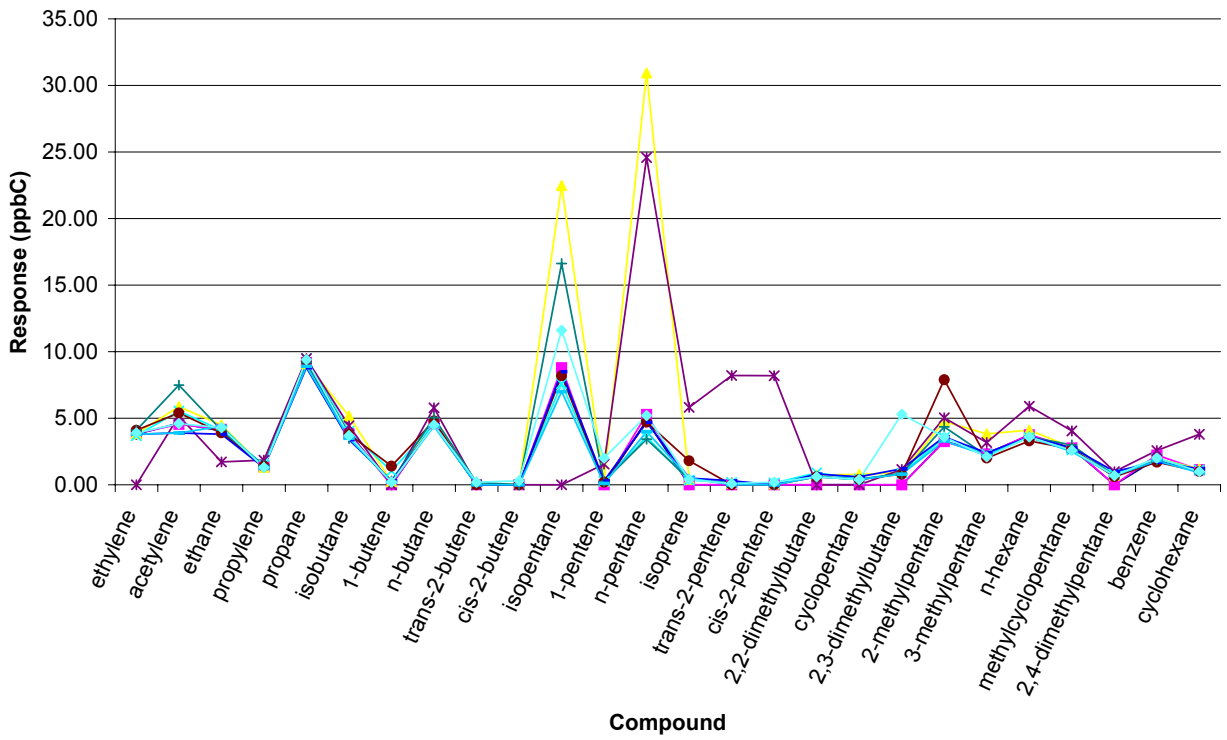
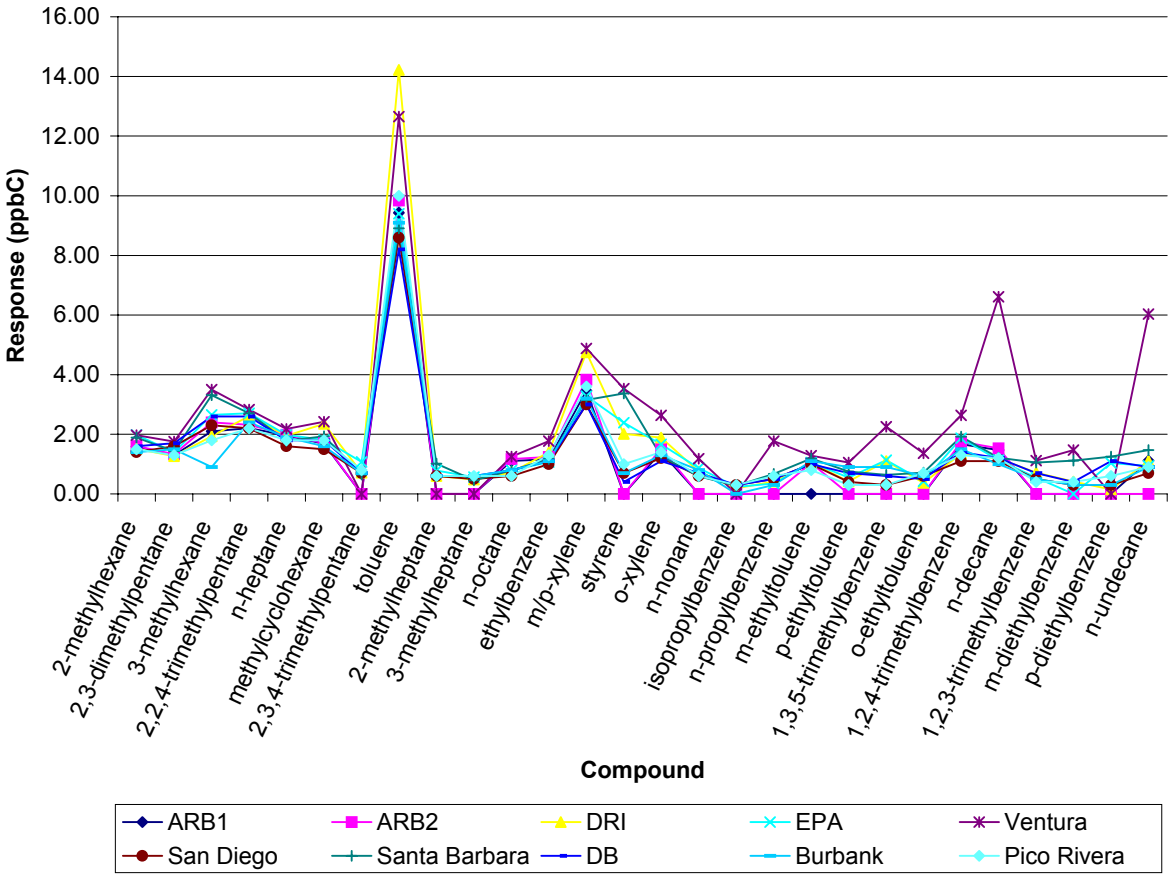


Figure D1. **1999 Whole Air Comparison Check (Continued)**



TTP continuous analyzer performance audits include audits of total NMHC analyzers (i.e., Bendix 8202a or Teco 55). Only 42 percent of the instruments audited were found to be operating within the ARB's control limits. The instruments operating outside the control limits were typically due to a blocked restrictor that shifted the timing window or retention time. The instruments found operating outside of the control limits were responsible for 1,766 days of lost data.

Table D2 shows the audit results for 1999. The purpose of this table is to estimate the accuracy of the hydrocarbon data that are on the database. The upper and lower probability limits represent the expected accuracy of 95 percent of all the analyzer's individual percent differences for all audit test levels at a single site. Consequently, audit results were not used in the statistical analysis if the audit was deleted due to an AQDA that resulted in data deletion.

***Table D2*. 1999 TTP Audits of Continuous Analyzer NMHC for PAMS Sites Under the CAPII**

Pollutant	Number of Analyzers Audited	Average % Difference	Probability Limits 95%UL	95%LL
NMHC	19	1.3	14.6	-3.1

Source: Quality Assurance Section, Accuracy Estimates

Performance audits were are also conducted on the flow rate of the PAMS carbonyl samplers. The audit results, shown in Table D3 below, indicate the PAMS carbonyl samplers as a group are able to maintain consistent and accurate flow rates. All instruments audited were found to be operating within the ARB's control limits. In previous years, problems with instruments operating outside the control limits were primarily due to improper calibration of the mass flow controllers. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site.

***Table D3*. 1999 Results for Carbonyl Sampler Performance Audits Conducted by ARB**

Pollutant	Number of Samplers Audited	Average % Difference	Probability Limits 95%UL	95%LL
Carbonyl	15	2.9	21.9	4.2

Source: Quality Assurance Section, Accuracy Estimates

Precision (field): Precision for the manual PAMS canister and aldehyde samplers is obtained through collocated sampling. Collocated sampling occurs at selected PAMS sites only. The data generated represent precision for the network as a whole. Each of the four participating PAMS laboratories selects one site where a duplicate canister of ambient air is collected using two separate sampling systems. In 1999, a collocated sampler was located at the Fresno-First site to represent the ARB network. The relative differences for regular/collocated comparisons ranged from 0.0% to 176.0%. Corrections were not made to the database based on the regular/collocated results.

In addition, daily duplicate analyses are performed by the laboratories on at least 10% of the total number of ambient samples. For the 1999 NMOC season, 156 daily duplicate samples were analyzed. The relative percent difference between the duplicate analyses were less than 15% for all target compounds that were measured at $\geq$ 5 times the reported limit of detection ($\geq$ 5 ppb C). This is well within the criteria of +/-25% recommended by the Technical Assistance Document for Analysis of Ozone Precursors (1998 TAD).

The precision of PAMS carbonyls data is also confirmed through collocated sampling in much the same manner as the canisters. The laboratory analyzes two collocated cartridges from one sampling system that has two sampling channels. In 1999, the collocated sampler was located at the Fresno-First site. The data for regular and

collocated analyses varied from 0.0% to 51.6%. Corrections were not made to the database based on the regular/collocated results.

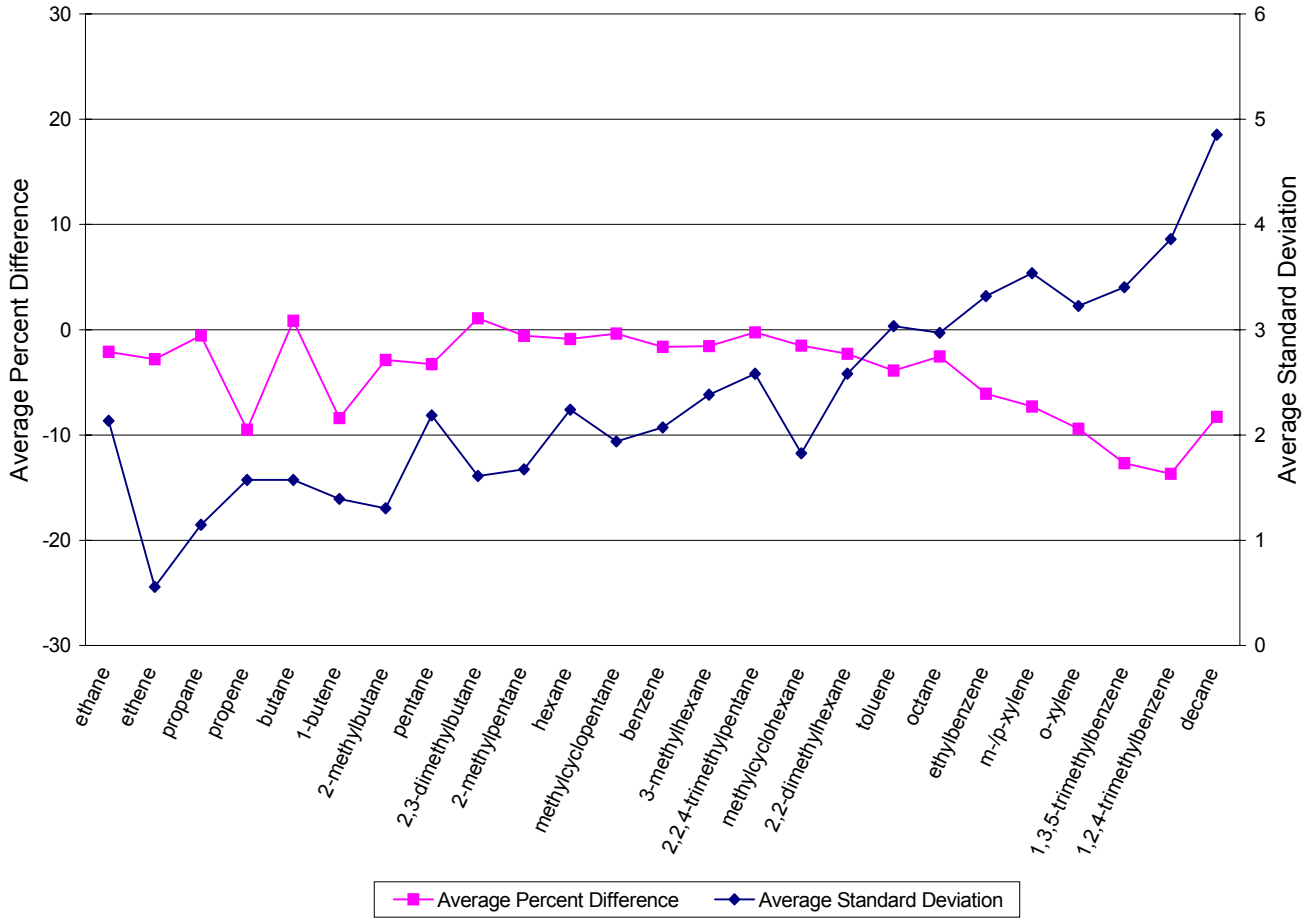
The laboratory also analyzes blank and spiked samples and performs duplicate analyses on 10% of the ambient samples. The blank data is obtained by attaching a cartridge to an unused channel of the sampler. A blank sample is collected for each scheduled trend day. The average blank values in 1999 were 0.01, 0.01, and 0.22 µg/5ml for formaldehyde, acetaldehyde, and acetone, respectively. Spiked samples are generally made at a frequency of one spike per analytical run and are done after the cartridges are desorbed. In 1999, the averages of the recoveries of the spiked samples were 107.2, 108.3 and 110.2% for formaldehyde, acetaldehyde, and acetone, respectively. The results were all within the acceptance criteria of 80-120%. Overall, the precision data indicates that the PAMS network is providing precise hydrocarbon and carbonyl data.

Motor Vehicle Exhaust Program

The motor vehicle exhaust program supports efforts to determine the reactivity of fuel components by speciating exhaust samples. The program provides hydrocarbon emissions data that can be compared against the regulatory standard for non-methane organic gases tail-pipe emissions, and a number of ozone precursors. Special studies are currently being conducted to determine emissions generated from vehicles operated under manufacturers recommendations. The data are included in a controlled data set, and are subject to formal data quality objectives.

Accuracy: The Southern Laboratory Branch analyzes exhaust samples collected on the dynomometer operated by the Mobile Source Control Division and Mobile Source Operations Division. Laboratory performance audits are conducted annually of the Southern Laboratory Branch for components of motor vehicle exhaust. The percent differences of the audit values and laboratory results shown here were calculated using the average reported concentration for each GC. Figure D1 illustrates the results for 1999. Overall, the laboratory performed well and provides accurate data to support the motor vehicle exhaust program. The laboratory continued to experience the typical low recovery rates for the heavier-end hydrocarbons.

Figure D2. **ARB's 1999 Motor Vehicle Exhaust Laboratory NMHC Audit Results**



E. Pesticides

Ambient and application pesticide monitoring is performed by the ARB at the request of the Department of Pesticide Regulation to determine the airborne concentration of pesticides at times and in areas of pesticide use. Some of the active ingredients found in pesticides are known to cause a wide range of adverse health effects in people, vegetation, and wildlife. The data are descriptive data sets, so are not subject to strict data quality objectives.

Two types of monitoring are conducted; ambient and application. During ambient, or community air measurements, ARB collects samples at approximately half a dozen locations (usually schools or other public buildings) in communities near agricultural areas expected to receive applications of the pesticide. Samples of 24 hours duration are typically collected for four days per week for four or more consecutive weeks. Application-site monitoring (e.g., sampling before and after a specific application), samples are collected immediately before, during, and for approximately 72 hours following pesticide application.

Accuracy (field): Since accurate measurement of pesticides in ambient air is dependent upon flow rate, flow audits are performed annually on pesticide samplers after calibration and prior to sampling to assure data quality. Table E1 represents the 1999 pesticide flow rate audit data. The flow audit results indicate that the network is providing accurate flow rate data.

Table E1. **ARB's 1999 Pesticide Flow Rate Audit Results**

Number of Samplers Audited	Average % Difference	Std Dev
120	-0.9	3.6

Precision (lab): Field quality control tasks are conducted for ambient and application monitoring to assess system precision for a variety of pesticides used. These tasks include: field spikes, trip spikes (standards), lab spikes and trip spikes, and replicate samples. In addition, collocated samplers are used and duplicate analyses are performed on 10 percent of the samples. The percent difference in 1999 for the duplicate analyses for application monitoring of atrazine ranged from 0.180% to 30.4%, with all but one duplicate pair less than 5% difference. All ambient duplicate analyses were below the estimated quantitation limit. The analytical precision results indicate that the network is providing precise pesticide data. Table E2 and E3 represent the field, trip, and laboratory spikes results for atrazine for ambient and application monitoring, respectively. Precision data for other pesticides monitored is available upon request.

Table E2. **ARB's 1999 Pesticide Ambient Field, Trip and Laboratory Spike Results for Atrazine**

QC Task	Number of Samples	Average % Recovery	Relative Std Dev
Field Spike	4	91.9%	4.21%
Trip Spike	4	92.0%	9.38%
Lab Spike	4	93.4%	3.18%

Source: Report for the Application and Ambient Air Monitoring for Atrazine

Table E3. **ARB's 1999 Pesticide Application Field, Trip, and Laboratory Spike Results for Atrazine**

QC Task	Number of Samples	Average % Recovery	Relative Std Dev
Field Spike	4	94.9	8.37
Trip Spike	4	97.0	6.18
Lab Spike	4	91.7	6.78

Source: Report for the Application and Ambient Air Monitoring for Atrazine

F. Consumer Products

Consumer products are chemically formulated products used by the public in homes and businesses. These compounds are reported to emit approximately 260 tons per day of smog-forming VOCs. Monitoring VOC levels in consumer products and finding ways to reduce VOC emissions they contain facilitates ARB's effort to reduce smog in the State. Consumer products are descriptive data sets. Although formal data quality objectives have not been established, effort is made by staff to ensure the accuracy and precision of the data. Visit the Consumer Products Program website at http://www.arb.ca.gov/consprod/consprod.htm.

Accuracy: The QAS does not conduct performance audits on the Consumer Product Program at this time. The Organics Laboratory, however, performs internal quality control checks to ensure the validity of the data produced. Below are tasks currently used by the laboratory to ensure precise data.

Precision (lab): Analytical precision is derived from duplicate analysis performed on 10% of the samples. The results from the analyses are compared, and for the sample to be valid, the percent difference must be less than 3%. Duplicate data that do not meet the criteria are deleted. Samples analyzed on the same date are also deleted. Following an investigation of the problem, samples are re-analyzed. Table F1 shows the duplicate data for the 2nd and 3rd quarter of 1999. Duplicate data for the 1st and 4th quarters are available upon request.

Table F1. **1999 Duplicate Final %VOC Results for 2nd and 3rd Quarter**

Sample Number	Dup 1 %VOC	Dup 2 %VOC	Percent Difference
1	96.60	96.60	0
2	12.80	13.30	0.5
3	33.50	35.20	1.7
4	27.20	27.00	0.2
5	99.60	99.80	0.6
6	17.70	15.40	2.3
7	81.80	81.20	0.6
8	87.10	88.10	1.0
9	9.00	8.10	0.9
10	7.90	9.20	1.3

Source: Special Analysis Section, Consumer Products Quality Control Report

The Consumer Product laboratory also analyzes known standards (trip standards) to establish control limits and limits of detection, runs system blanks to confirm the system is not contaminated, and conducts yearly multi-point calibrations to assess the instrument linearity. Presently, trip standards are not subject to meet established control limits or have corrective action(s) taken if a sample is out of the control range. The PE&S Section has recommended that these elements be added to enhance the value of trip standard as an assessment of precision. Overall, the analytical precision

results indicate that the network is providing precise consumer product data. Table F2 represents the trip standard results for the 2nd and 3rdquarters of 1999.

Table F2. **1999 ARB's Trip Standard Results for 2nd and 3rd Quarters**

Sample Number	% Difference from Target Value for:						
	Volatile Material wt. fraction	Water (KFO) wt. Fraction	Water (GC/TCD) wt. Fraction	Acetone wt. fraction	Methanol wt. fraction	Ethanol ft. fraction	%VOC (Total-Exempt)
1	0.0	1.3	-1.3	-6.0	-4.0	-7.0	3.0
2	-0.1	3.7	1.3	-16.0	-7.0	-8.0	0.0
3	0.0	0.3	-2.5	-3.0	0.0	-6.0	4.0
4	-0.1	5.3	2.2	-90.0	-89.0	-90.0	-14.5
5	0.0	0.7	2.0	-5.0	-3.0	-9.0	0.5
6	0.0	NA	3.0	-6.0	0.0	-5.0	-6.0
7	0.0	NA	2.2	-7.0	-5.0	-8.0	-3.0
8	0.0	NA	-0.3	-4.0	-4.0	-10.0	3.0
9	-0.1	NA	0.3	-14.0	-12.0	-18.0	5.5
10	-0.1	NA	0.3	-12.0	-10.0	-14.0	4.5
11	-0.1	8.3	-0.2	-28.0	-14.0	-9.0	1.5
12	0.0	-2.0	-1.0	-4.0	-2.0	-8.0	6.5
13	0.0	4.7	-2.0	-13.0	-11.0	-15.0	2.5

NA=analysis not run Source: Special Analysis Section, Consumer Products Quality Control Report

G. Meteorology

The ARB monitors meteorological parameters such as wind speed, wind direction, ambient temperature, relative humidity, barometric pressure, and total solar radiation. Real-time meteorological data are generated to characterize meteorological processes such as transport and diffusion, and to make air quality forecasts and burn-day decisions. The data are also used for control strategy modeling and urban airshed modeling. A State/local meteorology subcommittee of the Air Monitoring Technical Advisory Committee (AMTAC) agreed to define the level of acceptability for meteorological data as those used by the U.S. EPA for the Prevention of Significant Deterioration (PSD) program. The QAS audits to those levels.

The data variability collected by this element of the monitoring program are generally described as meeting or not meeting the PSD requirements. No mandatory corrections are made to the data. Even so, station operators are notified whether they passed the audit or not. Most operators make the effort to meet the audit standards. In 2001, the wind speed, wind direction and outside temperature data sets will be controlled data sets, subject to meeting PAMS objectives.

Accuracy (field): The accuracy of meteorological sensors are checked by annual performance audits. Overall, the network is performing well and providing extremely accurate meteorological data useful for airshed modeling and prescribing burn days. Visit http://www.arb.ca.gov/aaqm/met.htm for additional information. Table G1 summarizes the 1999 audit results. The average difference represents the combined differences from the certified value of all the individual audit points for each sensor. The

upper and lower probability limits represent the expected accuracy of 95 percent of all the single sensor's individual percent differences for all audit test levels at a single site.

***Table G1*. 1999 Results for Meteorological Sensor Performance Audits Conducted by ARB**

Sensor	Number of Sensors Audited	Average Difference	Probability Limits 95%UL	95%LL
Ambient Temp	78	0.0	0.5	-0.5
Horiz Wind Speed	82	0.4	3.4	-2.6
Relative Humidity	11	7.2	38.1	-23.7
Solar Radiation	1	9.7	11.1	8.3
Vert Wind Speed	7	0.0	0.2	-0.2
Wind Direction	83	-0.4	3.9	-4.7

Source: Quality Assurance Section, Accuracy Estimates

III. QUALITY CONTROL REPORTS

Quality Control (QC) reports are summaries of the quality control activities conducted by all MLD laboratories to support accurate and precise measurements. These activities include: duplicate, control, and spiked samples, limits of detection, calibrations, and audit results. All MLD QC reports are reviewed by the PE&S Section to verify that good laboratory practices were followed and to identify opportunities for data quality or process improvement. The PE&S Section makes suggestions, where appropriate, to help improve the overall quality and/or effectiveness of the data. QC reports are prepared quarterly, biannually, or annually, depending upon the program. Table 1 lists the QC reports submitted for review in 1999. At this time, QC reports are not prepared for the following programs: gaseous pollutants, pesticides, and meteorology.

***Table 1*. Quality Control Reports Submitted to PE&S Section for Review in 1999**

Submittal Frequency	Title of QC Report	Program (s) Supported
Quarterly	Special Analysis Section, Consumer Products	Consumer Products
Quarterly	Analysis of Motor Vehicle Exhaust	Motor Vehicle Exhaust
Quarterly	Analysis of Motor Vehicle Fuel	Motor Vehicle Exhaust
Quarterly	Inorganic Procedures	Particulate Matter
Quarterly	Organic Procedures	Toxics, Non-Methane Hydrocarbons
Annually	Non-Methane Organic Compounds	Non-Methane Hydrocarbons
Quarterly	Standards Laboratory	All

IV. STANDARDS LABORATORY

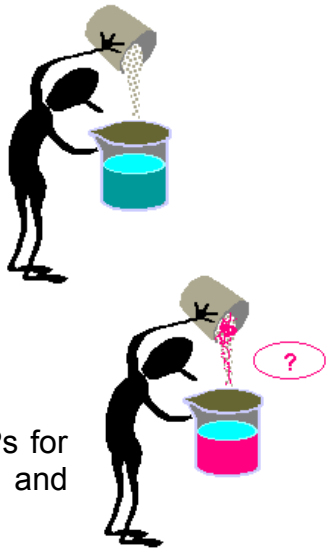
The Standards Laboratory, part of the PE&S Section, performs technical support and certification and verification services of calibration instruments, gases, and devices. Clients include ARB divisions, air districts, other states and countries, and private sector monitoring organizations. Calibrations and certifications are performed for ozone and flow rate transfer standards, certifications of compressed gas cylinders, and verifications of ozone and flow rate primary standards, to ensure that all are traceable to standards of the National Institute of Standards and Technology (NIST). A calibration establishes a correction factor to adjust or correct the output of an instrument, a certification establishes traceability of a transfer standard to a NIST-traceable standard, and a verification establishes comparability of a standard to a NIST-traceable standard of equal rank.

The Standards Laboratory also certifies and calibrates instruments used quarterly by the ARB's QA auditors. Table 1 shows the services and the volume of the services for 1999. For more information on the Standards Laboratory and the services they provide, visit the Certification of Standards website: http://www.arb.ca.gov/aaqm/qmosprog/stdslab/stdslab.htm.

Table 1. Standards Laboratory Services Provided for 1999

Service Provided	Number Conducted
Ozone Certifications	99
Ozone Verifications	41
Ozone Calibrations	2
Low Flow Certifications	431
Low Flow Verifications	19
Low Flow Calibrations	49
High Flow Certifications	64
Ambient Gas Cylinders Certified	227
Source Gas Cylinders Certified	205

V. LABORATORY STANDARD OPERATING PROCEDURES



Standard operating procedures (SOPs) are documents that provide step-by-step instructions for instrument operation. Each procedure has a specific method that each chemist and/or technician must follow to produce data-for-record. The SOPs are developed and published to ensure that, regardless of the person performing the operation, the results will be consistent. Most of the laboratory SOPs are available on the Internet at the following address: http://www.arb.ca.gov/aaqm/sop/summary/summary.htm.

Listed below in Tables 1, 2, 3, and 4 are the laboratory SOPs for particulate matter, toxic air contaminants, hydrocarbons, and consumer products, respectively.

Table 1. **Standard Operating Procedures for Analysis of Particulate Matter**

SOP	Title	Last Revision Date
MLD005	Acid Digestion and Analysis of Metals from the Total Suspended Particulates (TSP)	08/01/99
MLD007	PM10 Anions (SO4, NO3, Cl) by IC	01/19/88
MLD016	PM10 Filter Mass Analysis & Extraction for IC Analysis	03/21/91
MLD023	PM10 Cations (NH4 and K) by IC	02/01/88
MLD029	Dichotomous Filter Mass Analysis	04/24/91
MLD031	PM10 Filter Total Carbon Analysis	06/05/93
MLD033	TSP Anions (SO4) by IC	01/19/88
MLD034	Metals by X-Ray on Dichotomous & Xontech Filters	06/09/92

Table 2. **Standard Operating Procedures for Analysis of Toxic Air Contaminants**

SOP	Title	Last Revision Date
MLD022	Determination of Carbonyl Compounds in Ambient Air Using High Performance Liquid Chromatography	01/01/96
MLD028	Determination of Selected Polyaromatic Hydrocarbons (PAH) in Ambient Air	12/01/97
MLD050	Determination of Ambient Air Oxygenated Hydrocarbons Using SUMMA Canister Sampling and Gas Chromatography with Flame Ionization Detector	10/01/97
MLD051	Determination of 1,3 Butadiene and Benzene in Ambient Air by Capillary Column Gas Chromatography with Photoionization Detector	10/20/97
MLD052	Determination of Volatile Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography with Photoionization and Electron Capture Detectors.	10/01/94
MLD034	Metals by X-Ray on Dichotomous & Xontech Filters	06/09/92
MLD039	Extraction & Analysis of Hexavalent Chromium by IC	03/01/95

Table 3. **Standard Operating Procedures for Analysis of Hydrocarbons**

SOP	Title	Last Revision Date
MLD022	Determination of Carbonyl Compounds in Ambient Air Using High Performance Liquid Chromatography (HPLC)	01/01/96
MLD024	Determination of Total Non-Methane Organic Compounds by Pre-concentration Direct Flame Ionization Detection (PDFID)	09/15/99
MLD032	Determination of Non-Methane Organic Compounds in Ambient Air Using Gas Chromatography with Flame Ionization Detection	09/15/99

***Table 4*. Standard Operating Procedures for Consumer Products**

SOP	Title	Last Revision Date
MLD01	Standard Operating Procedure for the Total Volatile Measurement of Consumer Products	03/10/98
MLD02	Standard Operation Procedure for the Measurement of Ammonium Ion in Aqueous Consumer Products Using Ion Selective Electrode	03/10/98
MLD03	Standard Operating Procedure for the Karl Fischer (KF) Determination of Water with a KF Drying Oven in Consumer Products	03/10/98
MLD04	Standard Operating Procedure for Water Determination in Consumer Products Using Gas Chromatography	03/10/98
MLD05	Standard Operating Procedure for the Determination of Exempt Compounds in Aerosol Consumer Product Propellant by Gas Chromatography	03/10/98
MLD06	Standard Operating Procedure for the Determination of Exempt and Prohibited Compounds in Consumer Products by Headspace Gas Chromatography/Mass Spectrometry	03/10/98
MLD07	Standard Operating Procedure for the Determination of Acetone and Low Molecular Weight Alcohols in Consumer Products by Gas Chromatography - FID	02/03/99

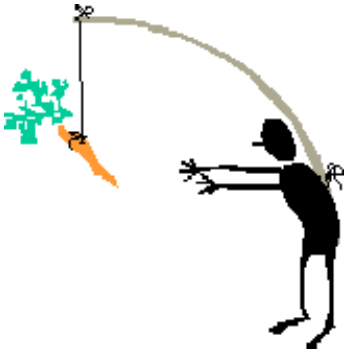
VI. PROGRAM CONTACTS

Program	Contact	Phone	Email
Gaseous Pollutants	Fred Burriell	(916) 327-0886	fburriel@arb.ca.gov
Particulate Matter	Sam Vogt	(916) 322-8919	svogt@arb.ca.gov
Toxic Air Contaminants	Tim Gergen	(916) 322-7053	tgergen@arb.ca.gov
Non-Methane Hydrocarbons	Merrin Bueto	(916) 323-0346	mbueto@arb.ca.gov
Pesticides	Don Fitzell	(916) 322-3892	dfitzell@arb.ca.gov
Consumer Products	Don Fitzell	(916) 322-3892	dfitzell@arb.ca.gov
Meteorology	Fred Burriell	(916) 327-0886	fburriel@arb.ca.gov

VII. UPCOMING ADDITIONS

This report will continue to evolve to include additional QA/QC measurements, new analyses of that information, and summary conclusions about the data meeting our clients' needs for stated objectives. Several elements we expect to include in the next annual issue of this report include:

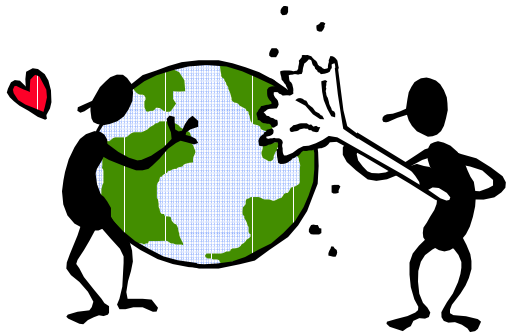
- Automated Reporting of Precision/Accuracy Results via Internet to Districts
- New QA Audits-TTP Carbonyl
- Siting Evaluations
- Ambient Air Interlaboratory Comparison for Toxics



APPENDIX A

AIR MONITORING NETWORK SURVEY

Quality Assurance Section
Monitoring and Laboratory Division



Gaseous Criteria Pollutant Monitoring as of November 9, 2001

Parameter Measured	Ozone	Nitrogen Dioxide	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide*
Sampling Schedule	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average
Number of ARB Sites	45	27	25	6	2
Number of District Sites	145	92	74	36	16
Number of Sites in Mexico	9	9	9	8	0
Method Used By ARB	Ultraviolet Photometry	Gas Phase Chemiluminescence	Non-Dispersive Infrared Photometry	Ultraviolet Fluorescence Detector	Thermal Oxidizer with Ultraviolet Fluorescence Detector
EPA Reference Method	Ultraviolet Photometry	Gas Phase Chemiluminescence	Non-Dispersive Infrared Photometry	Spectrophotometry (Pararosaniline Method)	Not Applicable
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Aerometric Information Retrieval System (AIRS)				

*Hydrogen Sulfide is only a State criteria pollutant. A Federal standard has not been set.

Hydrocarbon Monitoring as of November 9, 2001

Parameter Measured	**Non-Methane Hydrocarbon Compound (NMHC)**		**Continuous Non-Methane Hydrocarbons**	**Carbonyl Compounds**
	Total NMHC	Speciated NMHC (69 species, C2 through C12)		Acetone Formaldehyde Acetaldehyde
Sampling Schedule	Every 3 days, July through September plus episodes (3-hr samples)		Continuous Hourly Average	3-hr sampler
ARB Collection Method	XonTech 910A Gaseous Sampler with XonTech 912 Multisampler		Thermal Environmental (TECO) 55C Hydrocarbon Analyzer	Xontech 925 or other Carbonyl Samplers
Sampling Media	Polished Stainless Steel Canister		Not Applicable	DNPH-Coated Silica Gel Cartridges
Number of Sites Analyzed by the ARB	2 (High Ozone Areas)		3	2
Number of ARB Collocated Sites	1		0	0
Additional Sites Analyzed by other Agencies	7 SCAQMD (includes 2 continuous GC) 4 San Diego County APCD 6 San Joaquin Valley APCD 7 Ventura County APCD 1 Santa Barbara APCD		16	4 SCAQMD 2 San Diego County APCD 2 San Joaquin Valley APCD 1 Ventura County APCD 1 Santa Barbara APCD
ARB Analysis Method	Method 024 Cryofocusing Direct GC/FID	Method 032 Cryfocusing GC/FID	Flame Ionization Detector	Method 022 High-Performance Liquid Chromatography/Ultraviolet Detector
Laboratory Analyst	Sean Roy	Sean Roy, Barry Taylor	Not Applicable	Paul Chima
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Aerometric Information Retrieval System (AIRS)			

Particulate Matter Monitoring as of November 9, 2001

Parameter Measured	PM10 (0 - 10 microns)		Size Fractional PM10 (0 -2.5 and 2.5 - 10 microns)		PM2.5	
	Mass*	Nitrate, Sulfate, Chloride, Ammonium, Potassium	Mass (coarse and fine)	Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Ti, U, V, Y, Zn, Zr	Mass (fine)**	Speciated
Sampling Schedule	Every 6 days (24-hr samples) (Ag Burn sites every 3 days from Sep to Nov)		Every 6 days (24 hr samples)		Every 3 Days (Bakersfield and Fresno- First St sites everyday)	
ARB Collection Method	High Volume Selective Size Inlet Sampler		Dichotomous Selective Size Inlet Sampler		Mass Sequential & Single Channel	
Sampling Media	Quartz Microfiber Filter 8 x 10 inch		Teflon Filter 37 mm		Teflon Filter 46.2 mm	
Number of Sites Analyzed by the ARB	85* (Includes 14 sites in Mexico)	50 (Includes 13 sites in Mexico)	1	1	38**	0
Number of ARB Collocated Sites	5	6	1 (Fresno)	1 (Fresno)	9	0
Additional Sites Analyzed by other Agencies	15 BAAQMD* 34 SCAQMD* 4 SDAPCD* 93 other*	19 SCAQMD	0	0	76**	10***
ARB Analysis Method	Method 016 Electronic Analytical Balance	Method 007 and Method 023 Ion Chromatography	Method 029 Electronic Microbalance	Method 034 X-Ray Fluorescence	Method 055 Electronic Analytical Balance	
Laboratory Analyst	Yun Pan Scott Randall	Roxana Walker	Yun Pan, Scott Randall	Bill Davis	Janelle Ayeung	Betsy Ronsse
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)					

*These figures include 12 ARB (1 Mexico) and 50 District sites where PM10 mass is monitored continuously (1-hr averages) using TEOM, BAM, or Partisol.

**These figures include 11 ARB and 13 District sites where PM2.5 mass is monitored continuously (1-hr averages) using BAM.

***Analysis performed by EPA laboratory.

TSP and Visibility Monitoring as of November 9, 2001

Parameter Measured	**Total Suspended Particulates (TSP)**		**Coefficient of Haze**	**Relative Visibility**
	Lead	Sulfate	Particulates	Light Scatter
Sampling Schedule	Every 6 days (24 hr samples)	1 Every 12 days 4 Every 6 days 2 Every 3 days (24 hr samples)	2-Hour Average	Continuous Hourly Average
ARB Collection Method	High Volume Total Suspended Particulate Sampler		Optical Test Tape Sampler	Nephelometer
Sampling Media	Glass Fiber Filter 8 x 10 inch		Filter Tape	Not Applicable
Number of Sites Analyzed by the ARB	4 (Includes 1 site in Mexico)	4	23	8
Number of ARB Collocated Sites	1 (Bakersfield)	2 (Bakersfield, San Diego)	0	0
Additional Sites Analyzed by other Agencies	9 SCAQMD	13 SCAQMD	8	2
ARB Analysis Method	Method 005 Graphite Furnace Atomic Absorption/ ZEEMAN	Method 033 Ion Chromatography	Light Transmittance Through a Filter Tape	Scattering Coefficient of Light by Suspended Particles
Laboratory Analyst	Mike Humenny	Roxana Walker	Not Applicable	Not Applicable
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)			

Organic Toxic Air Contaminant Monitoring as of November 9, 2001

Parameter Measured	Volatile Organic Compounds (VOCs)			Polynuclear Aromatic Hydrocarbons (PAHs)
	Aromatic and Halogenated Compounds*	Methyltert-Butyl Ether (MTBE)	Ethanal (Acetaldehyde) Methanal (Formaldehyde) Butanone (Methylethyl- ketone)	Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Dibenz(a,h)anthracene Benzo(g,h,i)perylene Indeno(1,2,3-cd)pyrene
Sampling Schedule	Every 12 Days (24 hr samples)			
ARB Collection Method	XonTech 910A Gaseous Sampler		Xontech 920 Toxic Air Contaminant Sampler	High Volume Size Selective Inlet Sampler
Sampling Media	Polished Stainless Steel Canister		DNPH-Coated Silica Cartridges	Quartz Microfiber Filter 8 X 10 inch
Number of Sites Analyzed by the ARB	23 (2 in Mexico)		23	17
Number of ARB Collocated Sites	4 (Bakersfield, San Francisco, San Jose, Rubidoux)		2 (Bakersfield, Stockton)	2
Additional Sites Analyzed by other Agencies	18 BAAQMD		0	0
ARB Ana;ysis Method	Method 058 Cryogenic Trap Preconcentration Capillary GC/MS	Method 050 Cryogenic Trap Preconcentration Capillary GC/PID	Method 022 High-Performance Liquid Chromatography/ Ultraviolet Detector	Method 028 High-Performance Liquid Chromatography/ Fluorescence Detector
Laboratory Analyst	Ferry Niyati, Pam Gupta Ben Chang, Nati Lapurga	Lynn Yeung Cindy Chain	Paul Chima Dave Hartman	Dave Hartman
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)			

* Dichloromethane, trichoromethane, tetrachloromethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, bezene, toluene, styrene, 1, 2-dichlorobenzene, 1, 4-dichlorobenzene, o-xylene, m/p xylene, ethylbenzene, and 1,3-butadiene

Toxic Metals Monitoring as of November 9, 2001

Parameter Measured	Toxic Metals	
	Al, As, Ba, Br, Ca, Cl, Co, CR, Cu, Fe, Hg, K, Mn, Mo, Ni, p, Pb, Rb, S, Sb, Se, Si, Sn, Ti, U, V, Y, Zn, Zr	Chromium VI
Sampling Schedule	Every 12 Days (24 hr samples)	
ARB Collection Method	Xontech 920 Toxic Air Contaminant Sampler	
Sampling Media	Teflon Filter 37 mm	Cellulose Filter 37 mm
Number of Sites /Analyzed by the ARB	23	23
Number of Collocated Sites	2 (Bakersfield, Stockton)	2 (Bakersfield, Stockton)
Additional Sites Analyzed by other Agencies	0	0
ARB Analysis Method	Method 034 X-Ray Fluorescence	Method 039 Ion Chromatography
Laboratory Analyst	Bill Davis	Donald Taylor
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)	

Acid Deposition Monitoring as of November 9, 2001

Parameter Measured	Wet Deposition			Dry Deposition 0 - 2.5 microns				
	Conductance and pH	Nitrate, Sulfate	Ammonium Potassium Sodium	Mass	Nitric Acid	Chloride, Nitrate, Sulfate	Ammonium	Calcium Magnesium Potassium Sodium
Sampling Schedule	Continuous (Samples Collected Weekly)			Every 6 Days (24 hr samples)				
ARB Collection Method	Automatic Precipitation Sensor with Twin Buckets			Size Selective Particulate Sampler with Multiple Filters/Cartridges				
Sampling Media	Plastic Bucket			Teflon Filter	Nylon Filter	Teflon Filter	Teflon Filter	Teflon Filter
Number of Sites Analyzed by the ARB	5			0				
Number of ARB Collocated Sites	0			0				
Additional Sites Analyzed by other Agencies	1 SDAPCD 5 Other			5 Other				
ARB Analysis Method	Method 036 Conductivity and pH Meter	Method 037 Ion Chromatography	Method 037 Ion Chromatography	Method 041 Microbalance	Method 035 Automated Colorimetry	Method 044 Ion Chromatography	Method 046 Automated Colorimetry	Method 048 Atomic Absorption
Laboratory Analyst	George Dunstan			Nehzat Motallebi - Research Division				
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)							

Meteorological Monitoring as of November 9, 2001

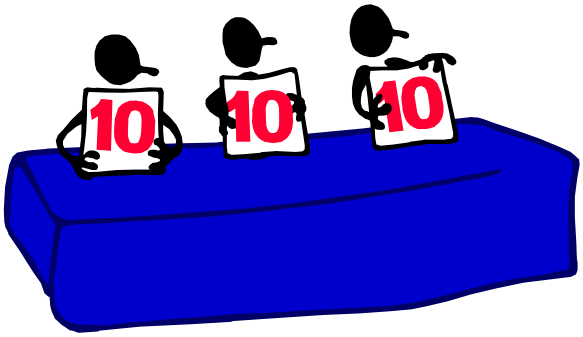
Parameter Measured	**Wind Speed**	**Wind Direction**	**Ambient Temperature**	**Relative Humidity**	**Atmospheric Pressure**	**Solar Radiati**
Sampling Schedule	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Averag
Number of ARB Sites	49	49	49	23	19	10
Number of District Sites	147*	139	112	56	32	39
Number of Mexico Sites	9	9	9	0	0	0
Method Used By ARB	Propeller or Cup Anemometer	Wind Vane Potentiometer	Aspirated Thermocouple or Thermistor	Thin Film Capacitor	Not Applicable	Thermopile o Pyranometer
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Aerometric Information Retrieval System (AIRS)					

* Includes 8 vertical wind speed sensors.

APPENDIX B

1999
DISTRICT USABLE DATA ANALYSIS

Quality Assurance Section
Monitoring and Laboratory Division



Precision Data Analysis By District For Usable Data - 1999

	Criteria Pollutants (%)					Particulate Samplers (%)							
District	CO	NO_2	O_3	SO_2	H_2S	PM2.5	PM10	PM10 Partisol	Dichot	TEOM	BAM	TSP	LEAD
Antelope Valley APCD	96	96	96							0			
Bay Area AQMD	100	100	89	99		0				66			0
California ARB	93	90	88	50		67	87		0	0			
Environmental Monitoring Company			100										
Glenn County APCD			65										
Great Basin Unified APCD					0	0	0	11		61			
Imperial County APCD	0	0	0	0	0						0		
Lake County APCD			92		0								
Mendocino County APCD	100	100	100			0							
Mojave Desert AQMD	87	73	93	83	96	75				0			
Monterey Bay Unified APCD	100	63	100	100		0							
National Park Service (NPS)			54										
Northern Sierra AQMD			100			75				0			
Northern Sonoma County APCD		0	100										
Placer County APCD			0										
Sacramento Metropolitan AQMD	92	89	92	92		51	90			59			
San Diego County APCD	65	85	91	82		48	0			0			
San Joaquin Valley Unified APCD	100	99	100				74						
San Luis Obispo County APCD		94	100	92		65				96			
Santa Barbara County APCD	100	90	92	81	0		56						
SEMARNAT (Mexico – Tracer Technologies)	12	12	0	2						0			
Shasta County APCD			72										
Siskiyou County APCD			98										
Sonoma Technology, Inc. (STI)		0	0							0			
South Coast AQMD	86	68	90	89		45	40			0	0	58	67
Tehama County APCD			4										
Ventura County APCD	70	98	99	96		70	70						
XonTech, Inc.			100	100	0		0						
Yolo-Solano APCD			92										

Note: ARB's goal for usable data is 85%.

References

1. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume I. Principles, EPA-600/9-76-005, January 1984.

2. Quality Assurance Handbook for Air Pollution Measure Systems. Volume II. Ambient Air Specific Methods, EPA-600/4-77-027a, May 1977.

3. State and Local Air Monitoring Network Plan, California Air Resources Board, May 1993.

4. Code of Federal Regulations, Title 40, Protection of the Environment, Part 58, Ambient Air Quality Surveillance (July 1992).

5. Air Monitoring Quality Assurance Manual. Volume I. Quality Assurance Plan, Monitoring and Laboratory Division, California Air Resources Board, February 1995.

6. Strategic Plan, California Air Resources Board, 1997.